

Application No. 09/867,227  
Response to Office Action of August 4, 2005

REMARKS/ARGUMENTS

Claims 15-19, 21-24, 34, and 35 are pending. Favorable reconsideration is respectfully requested in light of the Remarks below.

The rejection of Claims 15-19, 21-24, 34, and 35 under 35 U.S.C. §102 over US Patent No. 5,605, (US'); is traversed below. The below traversal of the outstanding rejection is organized by first reviewing the claimed invention in view of the disclosure U.S. ', followed by a presentation of how U.S. ' fails to disclose or suggest anywhere therein all aspects of the claimed invention, followed by a discussion of documents attached hereto that demonstrate that the process of making a crosslinked PMMA does not require a crosslinking agent; and therefore, it is impossible for crosslinked PMMA to contain a crosslinking agent each and every time it is made. Accordingly, the Office has failed to, and can not possibly, meet its burden required to sustain a rejection based upon inherency.

At best, US', discloses a media having a coating on one side of a film and optionally "polymeric beads such as crosslinked poly(methyl methacrylate)". As discussed below, US' fails altogether to disclose or suggest a product containing a crosslinking agent.

In direct contrast, the present invention relates, in part, to products having a cross-linking agent, at most 90 parts of colloidal inorganic particles(or submicron inorganic particles); and at least 10 parts of a polymeric binder, where the weight percentage of colloidal inorganic particles (or submicron inorganic particles) is greater than the weight percent of polymeric binder (see Claims 15, 34 and 35). Claims 15 and 34 relate to an ink receiving medium. Claim 35 relates to a microporous coating. Claim 34 further relates to situations where the colloidal inorganic particles are replaced with submicron inorganic particles.

It is recognized at page 2, paragraph 2, lines 3-6, of the Office Action that U.S. ' fails to set forth that the media disclosed therein contains a crosslinking agent. Since there is no

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explicit disclosure relied upon by the Office that provides that the composition according to US' contains a crosslinking agent, the Office apparently is taking the position that the composition according to US' "inherently" achieves this claimed state by disclosing that the composition optionally contains "polymeric beads such as crosslinked poly(methyl methacrylate)". However, the Office has provided no proof or specific disclosure within U.S.' demonstrating that media optionally containing "polymeric beads such as crosslinked poly(methyl methacrylate)" also contain a crosslinking agent. Rather, the Office is making a conclusion that inclusion of a crosslinking agent inherently results, which lacks any support whatsoever.

By definition, inherency is an admission that no explicit disclosure exists therein the cited references. As noted by the court in *In Re Ulrich*, 666 F.2d 578, 581, 212 USPQ 323 (CCPA 1981), the mere fact that a certain thing may result from a given set of circumstances is not sufficient to prove inherency. Inherency may not be established by probabilities or possibilities. Something that is inherent must inevitably be the result each and every time. It is by now well settled that the burden of establishing a prima facie case of anticipation resides with the Patent and Trademark Office. See *In Re Piasecki*, 745 F.2d 1468, 1472, 223 USPQ 785, 788 (Fed. Cir. 1984), quoting *In Re Warner*, 379 F.2d 1011, 1016, 154 USPQ 173, 177 (CCPA, 1967).

As noted by the Board of Patent Appeals and Interferences in *Ex parte Skinner*, 2 USPQ 2d 1788, before an Examiner can switch the burden of proof of showing non-inherency to the Applicant, the Office must provide some evidence or scientific reason to establish the reasonableness of the Office's belief that the functional limitation is an inherent characteristic of the prior art. In this case, the Office has provided no such evidence because the Examiner has not provided an adequate showing that the composition according to U.S. '736 contains a crosslinking agent each and every time.

In further support of Applicants' position, Applicants' respectfully direct the Examiner's attention to the documents attached hereto. The first document is Chapter 2, Part 1B, of a published Ph.D. thesis entitled "*Novel Carbazole Based Methacrylates, Acrylates,*

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*and Dimethacrylates to Produce High Refractive Index Polymers*" from Winola Lenore Rasmussen (see <<http://scholar.lib.vt.edu/theses/available/etd-12202001-135708/unrestricted/ThesisChapter2Part1B.PDF>>) from the Virginia Polytechnic Institute and State University. It demonstrates the many means by which methyl methacrylate, i.e. MMA, is able to be polymerized into poly(methyl methacrylate), i.e. PMMA, and further crosslinked to form crosslinked PMMA (such as that disclosed within U.S.). [See pages 30-47. A very large portion of this section explains the polymerization mechanisms of MMA (see pages 30-41) and crosslinked PMMA (see pages 42-47 and especially page 45, lines 17-18) via radical polymerization, induced thermally and/or by radiation (photocrosslinking).] Free radical polymerization and crosslinking does not require the presence of a crosslinking agent. In fact, page 31, line 9, admits that the free radical mechanism involved in MMA polymerization and PMMA crosslinking requires nothing other than the MMA monomers, including initiators. Thus, MMA polymerization and PMMA crosslinking does not require the presence of a crosslinking agent, especially if produced by photo-induced free radical polymerization where branched, propagating polymer chains combine and lead to a cross-linked polymer (See page 45, lines 17-18).

In light of the above, it is clear that one of ordinary skill in the art of polymerizing MMA and crosslinking PMMA recognizes that there are many means to obtaining a crosslinked PMMA. Such means include those that involve free radical mechanisms that are capable of being driven solely by radiation (i.e. photocrosslinking). Therefore, photo-induced free radical polymerization involve situations where only branched, propagating polymer chains combine and lead to a cross-linked polymer, i.e. crosslinked PMMA, in the absence of a crosslinking agent. Therefore, it is clear that one of ordinary level of skill in the art of polymerizing MMA and crosslinking PMMA recognizes that *not all crosslinked PMMA are made using a crosslinking agent; and therefore, not all crosslinked PMMA contain a crosslinking agent each and every time.*

In light of the above, U.S. ' fails to disclose that its composition contains a crosslinking agent each and every time which is required to establish a *prima facie* case of anticipation based on inherency (see *In Re Ulrich* discussed above). Further, the attached

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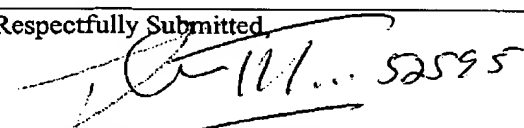
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documents actually evidence the fact that one of ordinary level of skill in the art recognizes that not all crosslinked PMMA contain a crosslinking agent each and every time. Therefore, the suggestion that a burden lies on the Applicant to refute a *prima facie* case of inherency is putting the cart before the horse because no *prima facie* case of inherency can possibly be sustained in light of the above reasons and the documents attached. Further, the document attached hereto demonstrates, in fact, that not all crosslinked PMMA contain a crosslinking agent each and every time; and therefore, it appears impossible that the Office can meet its burden to establish a *prima facie* case of anticipation based on inherency.

In summary and for all of the reasons stated above, withdrawal of these grounds of rejection is respectfully submitted.

Applicants respectfully submit that the present application is now in condition for allowance. Favorable reconsideration is respectfully requested. Should anything further be required to place this application in condition for allowance, the Examiner is requested to contact below-signed by telephone.

Please charge the amount of \$450.00 required for the request for extension of time to our Deposit Account No. 09-0525. In the event any variance exists between the amount enclosed and the Patent Office charges for filing the above-noted documents, including any fees required under 37 C.F.R. 1.136 for any necessary Extension of Time to make the filing of the attached documents timely, please charge or credit the difference to our Deposit Account No. 09-0525. Further, if these papers are not considered timely filed, then a petition is hereby made under 37 C.F.R. 1.136 for the necessary extension of time.

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	Thomas W. Barnes III, Ph.D. Registration No.	52,595

**etd<sup>vt</sup>s****Title page for ETD etd-12202001-135708**

<b>Type of Document</b>	Dissertation												
<b>Author</b>	Rasmussen, Winola Lenore												
<b>URN</b>	etd-12202001-135708												
<b>Title</b>	Novel Carbazole Based Methacrylates, Acrylates, and Dimethacrylate Refractive Index Polymers												
<b>Degree</b>	PhD												
<b>Department</b>	Chemistry												
<b>Advisory Committee</b>	<table><thead><tr><th>Advisor Name</th><th>Title</th></tr></thead><tbody><tr><td>Prof. James E. McGrath</td><td>Committee Chair</td></tr><tr><td>Prof. Timothy E. Long</td><td>Committee Member</td></tr><tr><td>Prof. Garth L. Wilkes</td><td>Committee Member</td></tr><tr><td>Prof. Harry Dorn</td><td>Committee Member</td></tr><tr><td>Prof. Judy Riffle</td><td>Committee Member</td></tr></tbody></table>	Advisor Name	Title	Prof. James E. McGrath	Committee Chair	Prof. Timothy E. Long	Committee Member	Prof. Garth L. Wilkes	Committee Member	Prof. Harry Dorn	Committee Member	Prof. Judy Riffle	Committee Member
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Prof. Garth L. Wilkes	Committee Member												
Prof. Harry Dorn	Committee Member												
Prof. Judy Riffle	Committee Member												
<b>Keywords</b>	<ul style="list-style-type: none"><li>• 13C NMR spectroscopy</li><li>• dimethacrylate</li><li>• refractive index</li><li>• 2-D COSY 1H NMR spectroscopy</li><li>• methacrylate</li><li>• thermal stability</li></ul>												

	<ul style="list-style-type: none"><li>• acrylate</li><li>• 9-(2</li><li>• molecular modeling</li><li>• carbazole epoxide</li><li>• 3-epoxypropyl)-carbazole</li></ul>
<b>Date of Defense</b>	2001-09-26
<b>Availability</b>	unrestricted

### Abstract

Homopolymers and copolymers produced from aromatic based methacrylates dimethacrylates are excellent materials with many applications in dentistry, optics, including optical eye wear, fiber optics, and non-linear optics, such as based polymers have demonstrated good optical, photo-refractive, and charge combined with ease of processing. The objective of this research was to design and characterize high refractive index polymers and copolymers for use in optical eyeglasses. Additionally, other interesting attributes were observed for selected polymers, such as high thermal stability and birefringence, which could lend to uses, such as non-linear optics and electronic data storage. A family of novel, homopolymers and copolymers were synthesized by incorporating carbazole, aromatic substituents, into methacrylates, acrylates, and dimethacrylates. Subsequent polymerizations provided for high refractive index materials well suited for lenses, spectacles and other applications.

The refractive index of materials can be increased by increasing the polarizable groups. By incorporating oxygen, sulfur, or sulfoxide groups into polymers, high refractive index polymers have been attained. By reacting the phenol, aromatic diols, or aromatic diols with 3-epoxypropyl)-carbazole, the refractive index of the final polymer can be increased. The reaction of the carbazole based intermediate with methacryloyl chloride or methacryloyl bromide eliminated any hydroxyl groups in the final methacrylate or dimethacrylate. The polymers do not undergo intermolecular hydrogen bonding, which increases viscosity. The absence of hydrogen bonding in the final methacrylated monomers reduces viscosity, which is desirable for processing.

Novel carbazole based monomers and polymers were characterized in terms of composition and molecular weight, thermal properties, such as melting point, glass transition temperature, and decomposition, and in terms of optical properties, such as refractive index. AIBN initiated carbazole-phenoxy based methacrylate polymerization was followed by FTIR, which showed the reaction to be completed within 40 minutes in DMA. DSC was used to determine the heat of polymerization ( $\Delta H_p$ ) for the carbazole-phenoxy based methacrylate, which was found to be  $-39.4$  kJ/mole. One and two dimensional

characterize the molecular structure of the carbazole-phenoxy based methacry carbazole-phenoxy based methacrylate homopolymer had a surprisingly high temperature.  $^{13}\text{C}$  NMR spectroscopy experiments and molecular modeling w the configuration of the polymerized carbazole-phenoxy based methacrylate. head linkages due to steric considerations could explain the higher thermal sta carbazole-phenoxy based methacrylate polymer.

Refractive indices of these carbazole based methacrylates, acrylates, and dim ranged from 1.53 to 1.63. Statistical copolymers of carbazole based methacry methacrylate were also produced by solution polymerization in DMAC, and c radical polymerization techniques, homopolymers and copolymers of the cart methacrylates, acrylates, and dimethacrylates were readily obtained. This rese variety of carbazole based chemistries which could produce controlled linear materials with high refractive index values and other interesting features.

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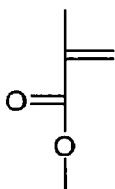
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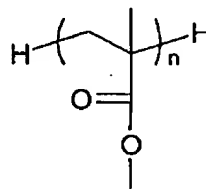
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### 2.3 Poly(methyl methacrylate) [9011-14-7]

Rohm and Bauer polymerized methyl methacrylate (MMA) [80-62-6] into transparent sheets in 1932.<sup>111</sup> Pure, atactic poly(methyl methacrylate) (PMMA) is an amorphous plastic with a high surface gloss, high brilliance, a clear transparency of 92 % (inorganic glass also has a transparency of 92 %), and a refractive index of 1.49. PMMA is classified as a hard, rigid, but brittle material, with a glass transition temperature of 105°C. PMMA has good mechanical strength, acceptable chemical resistance, and extremely good weather resistance. PMMA has favorable processing properties, good thermoforming, and can be modified with pigments, flame retardant additives, UV absorbent additives, and scratch resistant coatings.<sup>112,113</sup>



Methyl Methacrylate  
b.p. = 100°C



Poly(methyl methacrylate)

Because of the excellent optical properties, weather resistance, light weight, impact and shatter resistance (compared to inorganic glass), dimensional stability, heat resistance, and processability, PMMA has many profound and diverse uses that affect our lives every day. The ability to mold PMMA allows for the easy and inexpensive manufacture of complex optics. Complex reflex lenses, used in automobile tail lights, are made from PMMA. PMMA has been used for protection and safety in bank teller windows, as a barrier in police cars, in panels around hockey rinks, in storm doors, bath

<sup>111</sup> Stickler, M.; Rhein, T., "Polymethacrylates" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5<sup>th</sup> ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, 1992, A21, 473.

<sup>112</sup> Stickler, M.; Rhein, *ibid*.

<sup>113</sup> Kine, B.B; Novak, R.W., "Acrylic and Methacrylic Ester Polymers" in *Encyclopedia of Polymer Science and Engineering*, Wiley: New York, 1985, 262.

and shower enclosures, and in showcases.<sup>114,115</sup> For current safety glass applications, however, PMMA has been replaced by polycarbonates such as Lexan® and Merlon®.<sup>116</sup> Lenses, reflectors, and prisms are all made industrially from PMMA, mostly by casting.<sup>117,118</sup>

Health effects are minimal for PMMA.<sup>119</sup> For biomedical grade PMMA, however, there must be no residual monomer. Unlike PMMA, MMA is allergenic, and has health implications. PMMA has many biomedical uses because of its low *in-vivo* immune response. Anecdotically, PMMA was found to be extremely inert to tissues during World War II. Fighter pilots sometimes returned to base with, among other things, PMMA deeply embedded in them. PMMA was found to be very inert to surrounding tissues, even to the human eye, and shards that could not easily be removed were allowed to simply remain in place, coexisting with the surrounding tissue. PMMA is not biodegradable, thus it remained *in situ* throughout these pilots lives.<sup>120</sup>

Today, new derivatives of methacrylates, acrylates and dimethacrylates have biomedical applications in bone cements, dental fillings, and hard and soft contact lenses.<sup>121,122</sup> The biggest biomedical use of PMMA, again due to its excellent optical properties as well as its biomedical inertness, is in the human eye as a permanent implant for the intraocular lens following cataract surgery. Annually, 1.6 million intraocular lens implants are performed in the United States alone.<sup>123</sup> Sixteen million people are blinded

<sup>114</sup> Stickler, M.; Rhein, T., "Polymethacrylates" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5<sup>th</sup> ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, 1992, A21, 473.

<sup>115</sup> Kine, B.B; Novak, R.W., "Acrylic and Methacrylic Ester Polymers" in *Encyclopedia of Polymer Science and Engineering*, Wiley: New York, 1985, 262.

<sup>116</sup> Shultz, A., communication, 2001.

<sup>117</sup> Stickler, M.; Rhein, T., *Op. Cit.*

<sup>118</sup> Kine, B.B; Novak, R.W., *Op. Cit.*

<sup>119</sup> Stickler, M.; Rhein, T., *Op. Cit.*

<sup>120</sup> Chirila, T.; Hicks, C.; Dalton, P.; Vijayasekaran, S.; Lou, X.; Hong, Y.; Clayton, A.; Ziegelaar, B.; Fitton, J.H.; Platten, S.; Crawford, G.; Constable, I., *Prog. Polym. Sci.*, 1998, 23, 447.

<sup>121</sup> Stickler, M.; Rhein, T., *Op. Cit.*

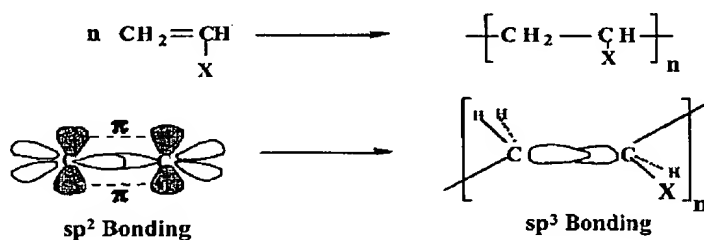
<sup>122</sup> Kine, B.B; Novak, R.W., *Op. Cit.*

<sup>123</sup> Newsletter, *Hospital Materials Management*, 2000, 25(9), 1.

by cataracts worldwide.<sup>124</sup> PMMA is also used to improve vision external to the body, again due to its excellent optical properties and processability, as well as its biomedical inertness when in contact with the eye, as contact lenses are. Hard and soft contact lenses, and optical spectacles for eyeglasses, are all made commercially from homopolymers and copolymers of PMMA.<sup>125,126</sup>

### 2.3.1 Polymerization of Methyl Methacrylate [80-62-6]

PMMA can be produced using a variety of polymerization mechanisms. The most common technique is the free radical polymerization of MMA. The free radical polymerization of acrylates and methacrylates is a chain polymerization across the double bond of the monomer (Figure 2.5). The free radical polymerization of MMA can be performed homogeneously, by bulk or solution polymerization, or heterogeneously, by suspension or emulsion polymerization. Free radical polymerizations can be performed relatively easily. Unlike many types of polymerizations, absolute dryness is not necessary. In order for polymerization to proceed successfully, however, all oxygen must be removed from the polymerization. Oxygen is a radical scavenger, and terminates free radical polymerizations.<sup>127,128</sup>



- Relief of Strain is a Driving Force
- Must be Activated

**Figure 2.6** Chain Polymerization for an Acrylate System<sup>129</sup>

<sup>124</sup> Charters, L., *Ophthalmology Times*, **2000**, 25(15), 1.

<sup>125</sup> Stickler, M.; Rhein, T., "Polymethacrylates" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5<sup>th</sup> ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, **1992**, A21, 473.

<sup>126</sup> Kine, B.B; Novak, R.W., "Acrylic and Methacrylic Ester Polymers" in *Encyclopedia of Polymer Science and Engineering*, Wiley: New York, **1985**, 262.

<sup>127</sup> Stickler, M.; Rhein, T., *Op. Cit.*

<sup>128</sup> Kine, B.B; Novak, R.W., *Op. Cit.*

<sup>129</sup> McGrath, J. E.; Wilkes, G.L.; Ward, T., *ACS Polymer Short Course Notes*, **2001**.

Radicals can be generated with radiation, heat, or chemical agents (usually in conjunction with radiation or heat). MMA can be polymerized spontaneously with heat. This polymerization is extremely slow, however, and of no industrial relevance. MMA has been polymerized anionically. The anionic polymerization is not used industrially because the monomer has to be extremely pure, and the polymerization must be performed at very low temperatures. The free radical polymerization of MMA is the predominant industrial mechanism to produce PMMA.<sup>130,131</sup>

### 2.3.1.1 Radiation Initiated Polymerization of MMA

The polymerization of MMA can be initiated with light or  $\delta$ -radiation. The photoinitiation of MMA, using ultraviolet or visible light, can be performed without sensitizers. It is still not entirely clear whether the photoinduced polymerization is by a free radical mechanism or by an excited state mechanism.<sup>132</sup> Typically, photochemically labile compounds called sensitizers are added. Some examples of photosensitizers are anthracene, t-butyl peroxide, benzoyl peroxide, 1-hydrocyclohexyl phenyl ketone, and azoisopropane. Figure 2.6 shows examples of various photoinitiators. The mechanism for the photoinitiation from benzophenone is shown in Figure 2.7. The formation of radicals from 1-hydrocyclohexyl phenyl ketone, also called Irgacure 184<sup>TM</sup>, is shown in Figure 2.8. Upon exposure to light, the sensitizer either forms free radicals directly, or is converted to an excited state before forming free radicals by abstracting a hydrogen atom from the monomer or solvent.<sup>133</sup> Radiation initiated polymerizations of MMA are typically performed as bulk polymerizations.<sup>134,135,136</sup>

<sup>130</sup> Stickler, M.; Rhein, T., "Polymethacrylates" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5<sup>th</sup> ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, 1992, A21, 473.

<sup>131</sup> Kine, B.B; Novak, R.W., "Acrylic and Methacrylic Ester Polymers" in *Encyclopedia of Polymer Science and Engineering*, Wiley: New York, 1985, 262.

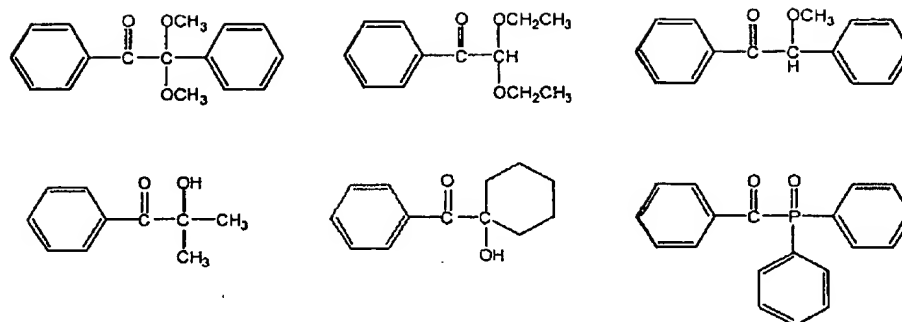
<sup>132</sup> Gruber, H.F., *Prog. Polym. Sci.*, 1992, 17, 953.

<sup>133</sup> Gruber, H. F. *ibid.*

<sup>134</sup> Decker, P., *Macromol. Symp.*, 1999, 143, 45.

<sup>135</sup> Stickler, M.; Rhein, T., *Op. Cit.*

<sup>136</sup> Kine, B.B; Novak, R.W., *Op. Cit.*



- Absence of benzylic radicals - reduces yellowing
- Clear coatings (low Abs. at 300-400 nm)

Figure 2.7 A. Examples of Photoinitiators and Their Advantages<sup>137</sup>

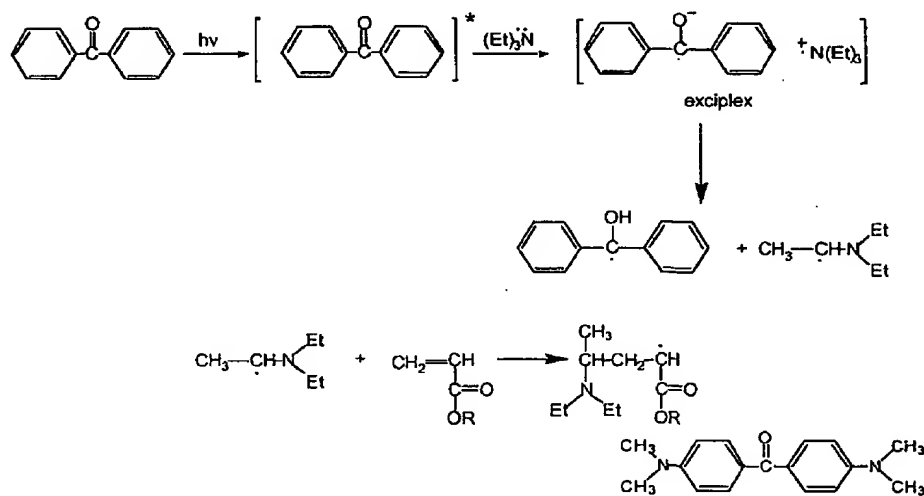
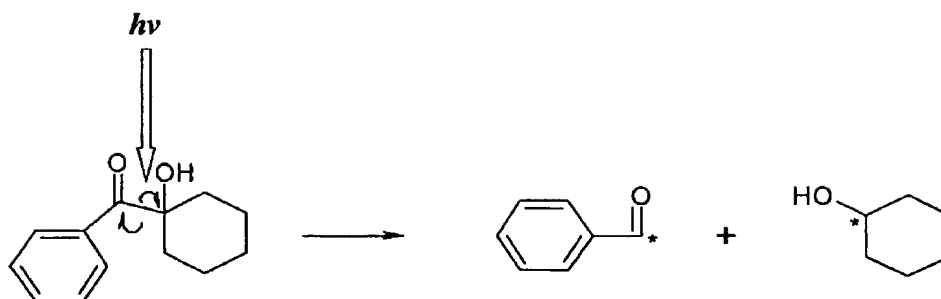


Figure 2.7 B. Photoinitiation Mechanism for Benzophenone<sup>138</sup>

<sup>137</sup> McGrath, J. E.; Wilkes, G.L.; Ward, T., *ACS Polymer Short Course Notes*, 2001.

<sup>138</sup> McGrath, J. E.; Wilkes, G.L.; Ward, T., *ibid*.



**Figure 2.8** Radical Formation of 1-Hydroxycyclohexyl Phenyl Ketone by UV Radiation

Light induced polymerization is considered one of the most efficient techniques for rapidly producing polymeric materials with well defined characteristics, particularly for cross-linked polymer networks. Photopolymerization is often the method of choice for rapid, assembly style, through-put polymerizations. Most of the photosensitive resins used in industrial photopolymerizations are made of acrylates rather than methacrylates, due to the much higher reactivity of the acrylate double bond. The propagation rate constant,  $k_p$ , is about 15,000 L/mole•second for acrylate monomers, which compares to less than 1,000 L/mole•second for methacrylate monomers.<sup>139</sup>

PMMA can also be produced by initiation with  $\delta$ -radiation, typically from a  $^{60}\text{Co}$  source, and by electron beams.  $\gamma$ -Radiation initiated polymerization is useful when the addition of an initiator is undesirable, or if the polymerization batch absorbs light too strongly, because of pigments or because of the monomer being impregnated into porous materials, such as wood or stone.<sup>140</sup>  $\gamma$ -Radiation is also used for sterilization purposes.  $\gamma$ -Radiation may be the polymerization mechanism of choice for polymers that must also be microbially sterile.

<sup>139</sup> Decker, P., *Macromol. Symp.*, **1999**, *143*, 45.

<sup>140</sup> Stickler, M.; Rhein, T., "Polymethacrylates" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5<sup>th</sup> ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, **1992**, *A21*, 473.

### 2.3.1.2 Heat Initiated Polymerization of MMA

The polymerization of MMA is most commonly initiated by thermally labile compounds, such as 2,2'-azobisisobutyronitrile (AIBN). The time for the concentration of initiator to decrease to one half of its original concentration is called the initiator half-life. A wide range of thermal initiators are available with appropriate half-lives at various polymerization temperatures. For example, AIBN has a half-life of 74 hours at 50°C, 4.8 hours at 70°C, and 7.2 minutes at 100°C.<sup>141,142</sup> t-Butyl peroxide has a half-life of 218 hours at 100°C, 34 hours at 115°C, and 6.4 hours at 130°C.<sup>143,144</sup> Upon heating, the thermal initiator forms free radicals, which initiate the polymerization. Figure 2.9 shows the generation of free radicals for benzoyl peroxide and AIBN. The equations for determining initiator half-life are shown in Figure 2.10. Scheme 2.1 shows initiation, propagation, and termination for the AIBN initiated polymerization of MMA.<sup>145</sup>

Free radical polymerization is a chain polymerization, and produces high molecular weight PMMA at low conversion. At all points in the conversion, only monomer, high polymer, and initiating species are detected. Allowing time for the polymerization to complete increases the overall polymer percent yield.<sup>146</sup>

Termination occurs through two mechanisms, combination and disproportionation (Scheme 2.1). With termination by combination, the resulting polymer has a head-to-head linkage, and the molecular weight roughly doubles. With termination by disproportionation, in which a proton is abstracted from one propagating chain end to another, two different types of polymers are produced with about the same molecular weight. Combination predominates at lower temperatures. Disproportionation becomes more significant at higher temperatures. The free radical polymerization of MMA at

<sup>141</sup> Odian, G., *Principles of Polymerization*, 2<sup>nd</sup> ed., Wiley: New York, 1981, 196.

<sup>142</sup> Brandrup, J.; Immergut, E.H.; Grulke, E.A. Eds., *Polymer Handbook*, 4<sup>th</sup> ed., Wiley: New York, 1999, II, 3.

<sup>143</sup> Odian, G., *Op. Cit.*, 196.

<sup>144</sup> Brandrup, J.; Immergut, E.H.; Grulke, E.A. Eds., *Op. Cit.*, II, 25.

<sup>145</sup> Odian, G., *Op. Cit.*, 179-242.

<sup>146</sup> Odian, G., *ibid.*

60° C has 79 % termination by disproportionation and 21 % termination by combination.<sup>147</sup> At higher temperatures, the incidence of chain transfer increases as well. With chain transfer, the propagating polymer radical reacts with another molecule by proton abstraction rather than by addition. When a proton is abstracted from another polymer molecule, this leads to branching and possible cross-linking.<sup>148</sup> Chain transfer to polymer is discussed in more detail in Section 2.3.2.

Thermally initiated polymerizations of MMA are performed as bulk polymerizations, solution polymerizations, suspension polymerizations, and emulsion polymerizations. The polymerization method used is determined by the application of the final polymer. Bulk polymerizations of MMA are still the predominant method for producing high quality acrylic glass, such as Plexiglas®. Solution polymerizations of MMA are used commercially to produce adhesives, paint resins, and additives. Suspension polymerizations of MMA produce PMMA beads, which can then be molded. Emulsion polymerizations of MMA are used to produce paint resins, paper coating agents and paper processing agents, textile binders, and additives.<sup>149,150</sup>

<sup>147</sup> Allcock, H.R.; Lampe, F.W., *Contemporary Polymer Chemistry*, 2<sup>nd</sup> ed., Prentice Hall: Englewood Cliffs, NJ, 1981, 61.

<sup>148</sup> Allcock, H.R.; Lampe, F.W., *ibid*, 59.

<sup>149</sup> Stickler, M.; Rhein, T., "Polymethacrylates" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5<sup>th</sup> ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, 1992, A21, 473.

<sup>150</sup> Kine, B.B; Novak, R.W., "Acrylic and Methacrylic Ester Polymers" in *Encyclopedia of Polymer Science and Engineering*, Wiley: New York, 1985, 262.

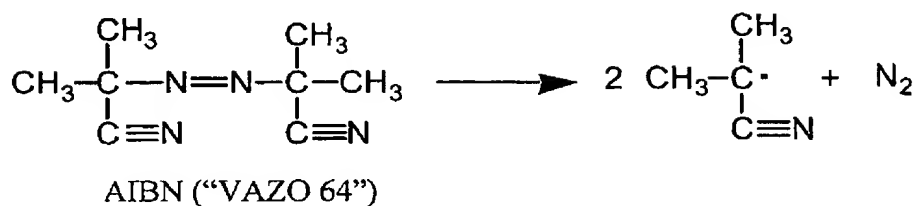
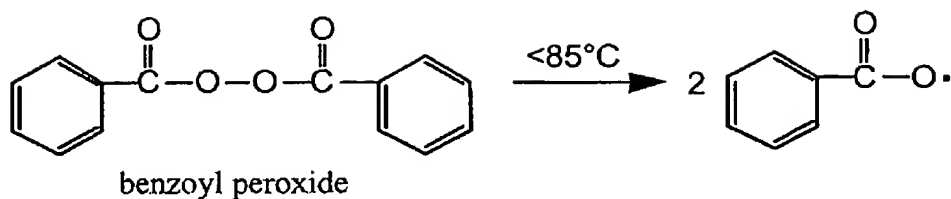
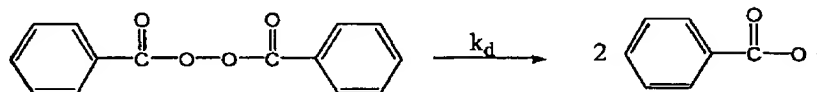


Figure 2.9 Generation of Free Radicals from Some Thermal Initiators



**Half-life:** The amount of time necessary for the initiator concentration to decrease to half its original value.

$[I_t]$  = initiator concentration at time  $t$   
 $[I_0]$  = initial initiator concentration  
 $k_d$  = disassociation rate constant

$$-\frac{d[I]}{dt} = k_d [I]$$

$$\frac{-d[I]}{[I]} = k_d dt$$

$$-\ln \frac{[I_t]}{[I_0]} = k_d t$$

$$\ln \frac{[I_0]}{[I_t]} = k_d t$$

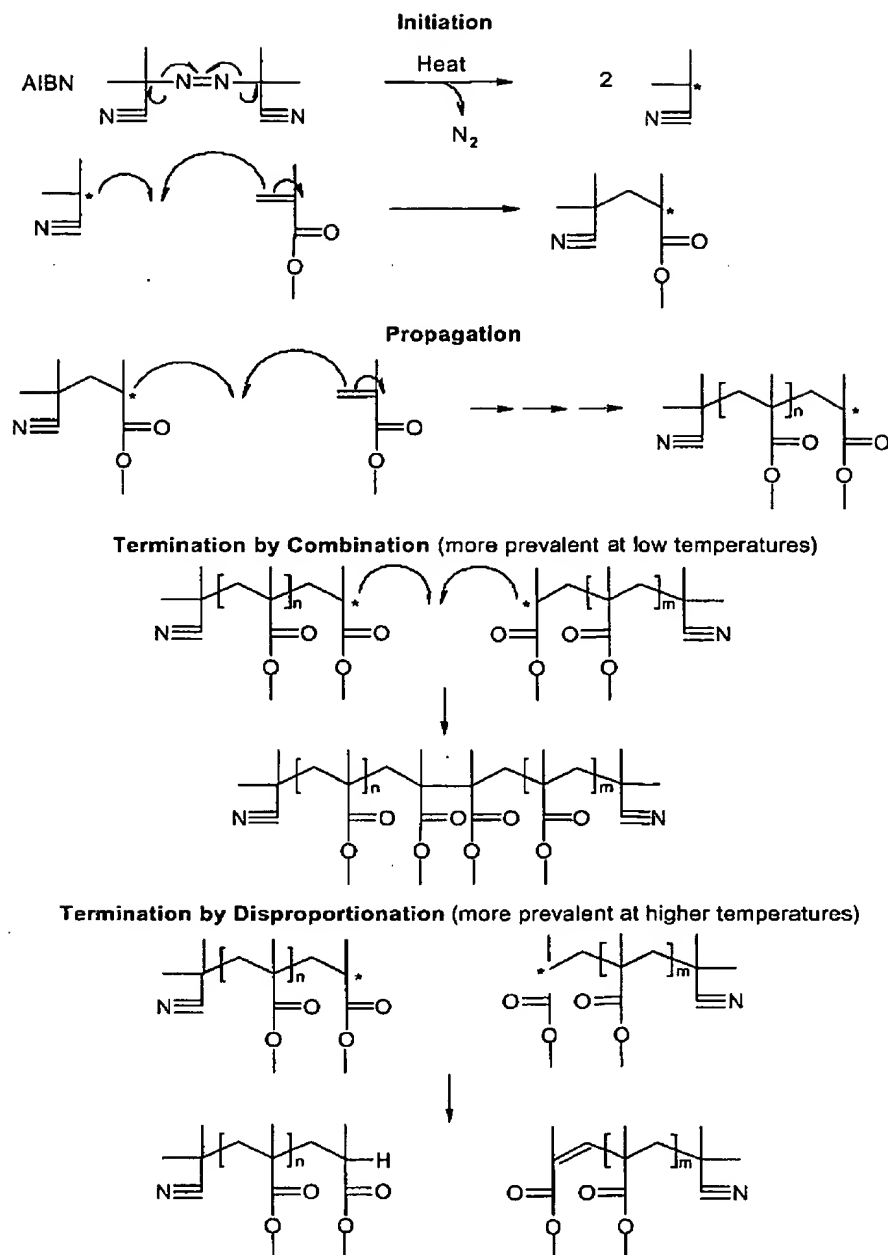
$$\ln 2 = k_d t_{1/2}$$

$$0.693 = k_d t_{1/2}$$

$$\frac{0.693}{k_d} = t_{1/2}$$

Figure 2.10 Rate of Free Radical Initiation<sup>151</sup>

<sup>151</sup> McGrath, J. E.; Wilkes, G.L.; Ward, T., *ACS Polymer Short Course Notes*, 2001.



**Scheme 2.1** Free Radical Polymerization of MMA Using AIBN<sup>152,153</sup>

<sup>152</sup> Odian, G., *Principles of Polymerization*, 2<sup>nd</sup> ed., Wiley: New York, 1981, 179-242.

<sup>153</sup> Allcock, H.R.; Lampe, F.W., *Contemporary Polymer Chemistry*, 2<sup>nd</sup> ed., Prentice Hall: Englewood Cliffs, NJ, 1981, 61.

### 2.3.1.3 Bulk Free Radical Polymerization and the Trommsdorf Effect

In bulk polymerizations, the monomer and initiator are combined undiluted. In large batches, exotherms due to autoacceleration are a concern. For most (non-radical) polymerizations, the reaction rate decreases with time. For the polymerization of MMA and other acrylic and vinylic monomers to high conversion, particularly in bulk polymerizations, the reaction rate can be governed by the gel effect, also called the Trommsdorf effect.<sup>154,155,156</sup>

In the first stage of the polymerization, Stage I, the polymerization rate is constant or declining with time. As the polymerization progresses to Stage II, the rate of polymerization increases with time, which can lead to dramatic autoacceleration, known as the gel or Trommsdorf effect. In the last stage of the polymerization, Stage III, the rate of polymerization is either constant or often declining. In bulk polymerizations, the extremely large increase in the viscosity of the reaction during Stage III can hinder the diffusion of the propagating polymer radicals. Even with these safety and viscosity drawbacks, bulk polymerizations are used commercially to produce high-gloss, optically clear acrylic glasses from MMA.<sup>157,158,159</sup>

### 2.3.1.4 Solution Free Radical Polymerization

By polymerizing MMA in a solvent, many of the disadvantages of the bulk polymerizations are overcome. The solvent acts as a diluent and aids in the transfer of heat of polymerization. Thermal control is much better in solution polymerizations

<sup>154</sup> Stickler, M.; Rhein, T., "Polymethacrylates" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5<sup>th</sup> ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, 1992, A21, 473.

<sup>155</sup> Kine, B.B; Novak, R.W., "Acrylic and Methacrylic Ester Polymers" in *Encyclopedia of Polymer Science and Engineering*, Wiley: New York, 1985, 262.

<sup>156</sup> Odian, G., *Principles of Polymerization*, 2<sup>nd</sup> ed., Wiley: New York, 1981, 271.

<sup>157</sup> Stickler, M.; Rhein, T., *Op. Cit.*

<sup>158</sup> Kine, B.B; Novak, R.W., *Op. Cit.*

<sup>159</sup> Odian, G., *Op. Cit.*, 286-287.

compared to bulk polymerizations. Additionally, the viscosity of the reaction mixture is decreased.<sup>160,161</sup>

The solvent must be chosen with care, however. Many organic solvents acts as chain transfer agents for free radical reactions, thus lowering the polymer molecular weight. Aromatic solvents can accept and stabilize a free radical, in effect inhibiting the polymerization.<sup>162</sup> For solution polymerizations of MMA, N,N-dimethylacetamide and dimethylformamide are examples of acceptable solvents. Chain transfer is discussed in detail in Section 2.3.2.

#### 2.3.1.5 Suspension Polymerization

Small beads of PMMA can be readily produced using suspension polymerization. The monomer is stirred with approximately twice its volume of water and dispersants. This forms a droplet like suspension of the monomer phase in the aqueous phase. Dispersants stabilize the polymerization and prevent the droplets from adhering to one another. Dispersants are water soluble compounds such as gelatin, cellulose derivatives, or water soluble polymers like poly(vinyl alcohol). Dispersants can also be finely suspended inorganic compounds, such as kaolin, magnesium carbonate, or aluminum hydroxide. The bead or particle size can be controlled by choosing appropriate stirring conditions and dispersants, to produce beads ranging from 50  $\mu\text{m}$  to 1000  $\mu\text{m}$ .<sup>163</sup>

Suspension polymerization is initiated with free radical initiators that favor the monomer phase, such as benzoyl peroxide. Suspension polymerization provides for the removal of heat from the polymerization by the aqueous phase, while allowing for high polymerization rates in the monomer phase (Figure 2.11). After completion of the

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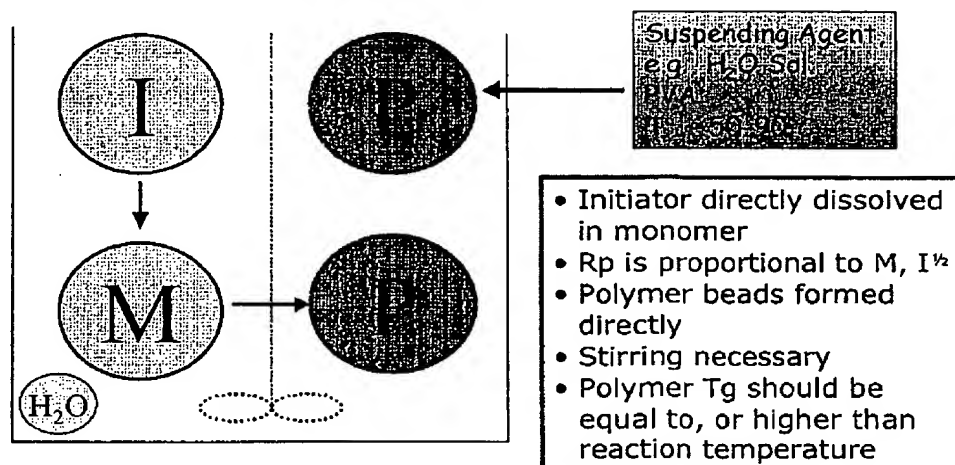
<sup>160</sup> Stickler, M.; Rhein, T., "Polymethacrylates" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5<sup>th</sup> ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, 1992, A21, 473.

<sup>161</sup> Kine, B.B; Novak, R.W., "Acrylic and Methacrylic Ester Polymers" in *Encyclopedia of Polymer Science and Engineering*, Wiley: New York, 1985, 262.

<sup>162</sup> Odian, G., *Principles of Polymerization*, 2<sup>nd</sup> ed., Wiley: New York, 1981, 242-243.

<sup>163</sup> Stickler, M.; Rhein, T., *Op. Cit.*

polymerization, the PMMA polymer beads are easily separated from the aqueous phase by filtration, washed with water, and dried.<sup>164</sup>



#### • ADVANTAGES

- Can easily recover polymer by filtration of beads
- Water normally used as the medium: environmentally friendly, inexpensive, good heat transfer
- Bead size is controllable
- Viscosity is not a problem

#### • DISADVANTAGES

- Can only be used effectively for glassy materials (not low  $T_g$  materials)

Figure 2.11 Suspension Polymerization<sup>165</sup>

<sup>164</sup> Stickler, M.; Rhein, T., "Polymethacrylates" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5<sup>th</sup> ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, 1992, A21, 473.

<sup>165</sup> McGrath, J. E.; Wilkes, G.L.; Ward, T., *ACS Polymer Short Course Notes*, 2001.

### 2.3.1.6 Emulsion Polymerization

Emulsion polymerization is used to make colloidal dispersions of PMMA. Emulsion polymerization involves the free radical polymerization of monomers that are in a colloidal suspension. Surfactants are added to the (typically) aqueous phase to form micelles. The free radical initiators used are water soluble, such as potassium persulfate. Monomer, including a fraction of free radical initiated monomer, migrates to the micelles. Within the micelles, the monomer concentration is very high, and this is where the polymerization takes place. Under optimal conditions, theoretically, there is one propagating chain end per micelle. Emulsion polymerization provides for high conversion and very high molecular weight polymer within the micelles. Figure 2.12 depicts an emulsion polymerization. The dispersed PMMA particles produced are very small, ranging from 0.001  $\mu\text{m}$  to 0.100  $\mu\text{m}$ .<sup>166,167</sup> Emulsion polymerizations of MMA are used to produce paint resins, paper coating agents and paper processing agents, textile binders, and additives.<sup>168</sup>

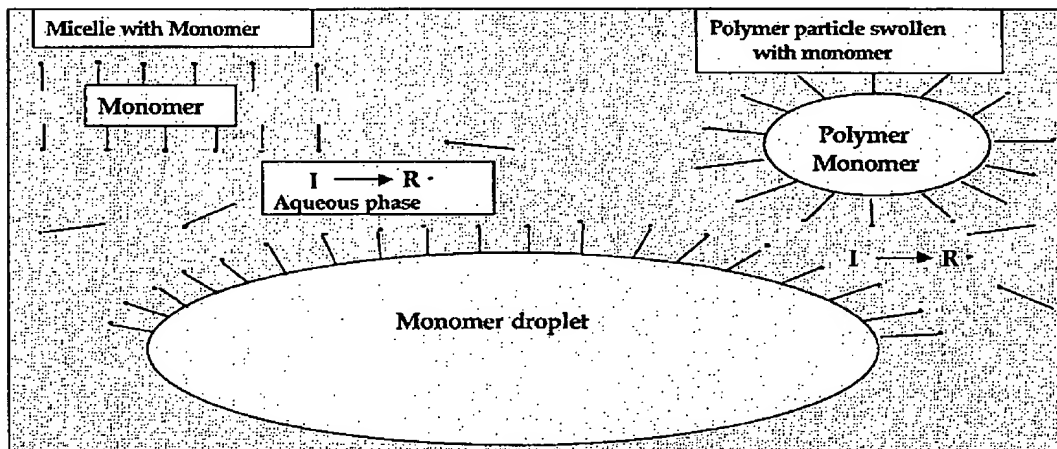


Figure 2.12 Emulsion polymerization<sup>169</sup>

<sup>166</sup> Stickler, M.; Rhein, T., "Polymethacrylates" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5<sup>th</sup> ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, 1992, A21, 473.

<sup>167</sup> Odian, G., *Principles of Polymerization*, 2<sup>nd</sup> ed., Wiley: New York, 1981, 334-335.

<sup>168</sup> Stickler, M.; Rhein, T., *Op. Cit.*

<sup>169</sup> McGrath, J. E.; Wilkes, G.L.; Ward, T., *ACS Polymer Short Course Notes*, 2001.

### 2.3.2 Chain Transfer

Chain transfer is the premature termination of a growing polymer chain and the initiation of another polymer chain by the transfer of a hydrogen, or other atom or species, to the growing polymer chain from some compound present in the system, which could be the monomer, initiator, solvent, or polymer. The radical displacement reaction, shown below, is called a chain transfer reaction.<sup>170,171</sup> Chain transfer to the initiator is referred to as induced initiator decomposition.<sup>172</sup>

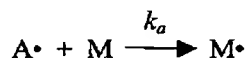


where  $XA$  = monomer, initiator, solvent, or other species

$X$  = atom or species transferred

$k_{tr}$  = chain transfer rate constant

The new free radical  $A^{\bullet}$ , reinitiates the free radical polymerization. This causes the



where  $k_a$  = rate constant for reinitiation of polymerization

polymer molecular weight to be lower than predicted. Chain transfer is a chain breaking reaction, which leads to a decrease in the length of the polymer chains. The number of propagating chain ends remains constant, however.<sup>173</sup>

When reinitiation is rapid, with no change in the polymerization rate, in other words, the chain reinitiation rate constant  $k_a$  is approximately equal to the propagation rate constant  $k_p$ , then two different scenarios can occur. In the first case, when the chain transfer rate constant is much slower than the propagation rate constant ( $k_p \gg k_{tr}$ ), this is

<sup>170</sup> Odian, G., *Principles of Polymerization*, 2<sup>nd</sup> ed., Wiley: New York, 1981, 226.

<sup>171</sup> Allcock, H.R.; Lampe, F.W., *Contemporary Polymer Chemistry*, 2<sup>nd</sup> ed., Prentice Hall: Englewood Cliffs, NJ, 1981, 61.

<sup>172</sup> Odian, G., *Op. Cit.*, 226.

<sup>173</sup> Odian, G., *ibid.*

considered the normal mode of chain transfer, where the molecular weight of the polymer chains is decreased. In the second case, when the chain transfer rate constant is much larger than the propagation rate constant ( $k_p \ll k_{tr}$ ), the molecular weight is drastically reduced, and the resulting polymers are referred to as telomers. In both cases, the overall rate of polymerization remains constant.<sup>174</sup>

When reinitiation is slow compared to propagation ( $k_a < k_p$ ), there is a decrease in both the molecular weight and the rate of polymerization. When the chain transfer rate constant is much slower than the propagation rate constant ( $k_p \gg k_{tr}$ ), then this effect is called retardation.<sup>175,176</sup> When the chain transfer rate constant is much larger than the propagation rate constant ( $k_p \ll k_{tr}$ ), then there is a large decrease in the molecular weight and in the rate of polymerization,  $R_p$ , and this effect is known as degradative chain transfer.<sup>177,178</sup>

For clarification, inhibitors stop every radical, and the polymerization completely stops until the inhibitor is consumed. Retarders are less effective, and only stop a portion of the radicals. The difference between inhibitors and retarders is a matter of degree.<sup>179</sup> Oxygen, for example, is a well known and powerful inhibitor. Oxygen reacts with radicals to form relatively unreactive peroxy radicals, which reacts with itself or other propagating radicals to form inactive products.<sup>180,181,182</sup> In addition, oxygen has one of the largest ratios of  $k_{tr}/k_p$ , which for methyl methacrylate at 50°C is 33,000, making oxygen an extremely effective inhibitor.<sup>183,184</sup> For this reason, acrylates and

<sup>174</sup> Odian, G., *Principles of Polymerization*, 2<sup>nd</sup> ed., Wiley: New York, 1981, 226.

<sup>175</sup> Odian, G., *ibid.*, 226, 242-251.

<sup>176</sup> Flory, P., *Principles of Polymer Chemistry*, Cornell University Press: Ithaca, 1953, 161-174.

<sup>177</sup> Odian, G., *Op. Cit.*.

<sup>178</sup> Flory, P., *Op. Cit.*

<sup>179</sup> Odian, G., *Op. Cit.*, 242.

<sup>180</sup> Odian, G., *ibid.*, 249.

<sup>181</sup> Maybod, H.; George, M.H.; *J. Polym. Sci. Polym. Chem. Ed.*, 1977, 15, 693.

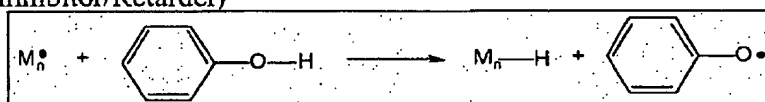
<sup>182</sup> George, M.H.; Ghosh, A., *J. Polym. Sci. Polym. Chem. Ed.*, 1978, 16, 981.

<sup>183</sup> Odian, G., *Op. Cit.*, 246.

<sup>184</sup> Eastmond, G.C., "Kinetic Data for Homogeneous Free Radical Polymerizations of Various Monomers," in *Comprehensive Chemical Kinetics*, Bamford, C.H.; Tipper, C. Eds., Elsevier: New York, 1976, 14A, 132.

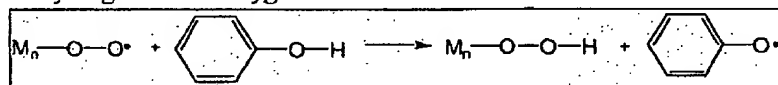
methacrylates are typically stored under oxygen, rather than nitrogen or argon. Prior to polymerization, oxygen can be removed by mild vacuum, followed by a nitrogen gas purge (repeated several times), or by careful distillation over a nitrogen atmosphere. Other inhibitors that may be present to ensure safe storage, such as monomethyl ester hydroquinone (MEHQ), can be removed prior to polymerization by careful distillation over a nitrogen atmosphere, or by passing through a inhibitor removal column containing basic silica or inhibitor removal beads, which are commercially available through Aldrich and other chemical suppliers.<sup>185</sup> Figure 2.13 depicts several types of inhibitors.

**Phenols: (Inhibitor/Retarder)**

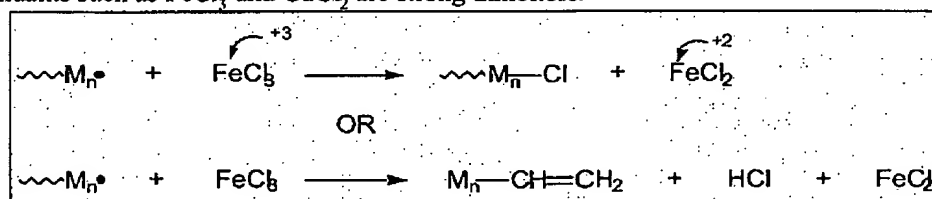


•Electron donating groups at the ortho positions can make this a better inhibitor.

•Phenol can be synergistic with oxygen as an inhibitor.



•Oxidants such as  $\text{FeCl}_3$  and  $\text{CuCl}_2$  are strong inhibitors.



**Figure 2.13** Types of Inhibitors<sup>186</sup>

The degree of polymerization, and thus the number average molecular weight,  $\langle X_n \rangle$ , is dependent upon the effects of all possible chain transfer reactions within the polymerization, such as monomer, chain transfer agents, which could be solvent, and initiator. This relationship can be expressed by the Mayo Equation (Equation 2.8). The chain transfer constant,  $C$ , is the constant for that particular substance,  $k_{tr}$ , to the

<sup>185</sup> Shobha, H.; Sankarapandian, M.; Uhrich, K.; Rasmussen, L., conversations/experience, 1999.

<sup>186</sup> McGrath, J. E.; Wilkes, G.L.; Ward, T., *ACS Polymer Short Course Notes*, 2001.

propagation rate constant  $k_p$ . The chain transfer constants for monomer, chain transfer agent, and initiator are  $C_M$ ,  $C_S$ , and  $C_I$ , respectively.<sup>187,188,189</sup> The  $C_M$  at 60°C for methyl methacrylate is  $0.07\text{--}0.25 \times 10^{-4}$ .<sup>190,191,192</sup> The  $C_S$  for chloroform in a methyl methacrylate polymerization at 80°C is  $1.7 \times 10^{-4}$ .<sup>193</sup>

$$\frac{1}{\langle X_n \rangle} = \frac{k_t R_p}{k_p^2 [M]^2} + C_M + C_S \frac{[S]}{[M]} + C_I \frac{k_t R_p^2}{k_p^2 f k_d [M]^3} \quad \text{Equation 2.8}$$

$$\text{where } C_M = \frac{k_{tr,M}}{k_p} \quad C_S = \frac{k_{tr,S}}{k_p} \quad C_I = \frac{k_{tr,I}}{k_p}$$

$\langle X_n \rangle$  = number average molecular weight

$[S]$  = concentration of chain transfer agent

$[M]$  = concentration of monomer

$k_t$  = termination rate constant

$f$  = initiator frequency (fraction of radicals produced in the reaction that initiates polymer chains)

$k_d$  = initiator decomposition rate constant

Another phenomenon that must be considered is chain transfer to another polymer molecule. Chain transfer to polymer forms a free radical propagating site on a polymer chain. The subsequent polymerizations of monomer leads to the production of a branched polymer (Figure 2.14). Termination by combination of branched, propagating polymer chains can lead to a cross-linked polymer. Chain transfer to polymer is more of a consideration at high or complete conversions. Branching and cross-linking greatly

<sup>187</sup> Odian, G., *Principles of Polymerization*, 2<sup>nd</sup> ed., Wiley: New York, 1981, 227.

<sup>188</sup> Flory, P., *Principles of Polymer Chemistry*, Cornell University Press: Ithaca, 1953, 138.

<sup>189</sup> Heuts, J.; Davis, T.P.; Russell, G.T., *Macromolecules*, 1999, 32, 6019.

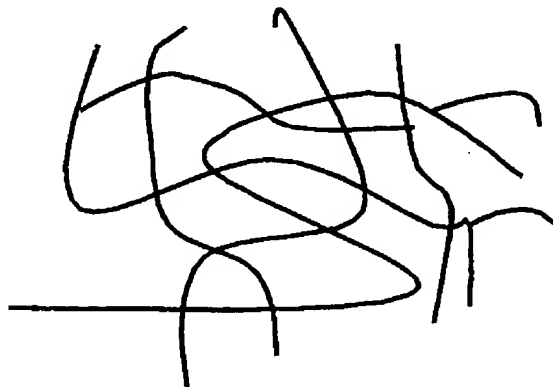
<sup>190</sup> Brandrup, J.; Immergut, E.H.; Grulke, E.A. Eds., *Polymer Handbook*, 4<sup>th</sup> ed., Wiley: New York, 1999, V, 88.

<sup>191</sup> Ayrey, G.; Haynes, A.C., *Makromol. Chem.*, 1974, 175, 1463.

<sup>192</sup> Stickler, M.; Meyerhoff, G., *Makromol. Chem.*, 1978, 179, 2729.

<sup>193</sup> Rudin, A., *The Elements of Polymer Science and Engineering*, Academic Press: New York, 1982, 219.

effect the physical properties of a polymer. Branching drastically reduces the crystallinity of a polymer; cross-linking causes the polymer to be infusible.<sup>194</sup>



**Figure 2.14** Cross-linked Polymer, with Branches

The branching density,  $\rho$ , can be expressed as a function of the polymer transfer constant,  $C_P$ , and the extent of the polymerization reaction,  $p$  (Equation 2.9).<sup>195</sup>

$$\rho = -C_P[1 + (1/p)\ln(1-p)] \quad \text{Equation 2.9}$$

The branching density is the number of branches per molecule polymerized. Particularly for poly(ethylene), poly(vinyl acetate), and poly(vinyl chloride) (PVC), the extent of branching can be varied considerably by controlling the polymerization temperature and other reaction considerations.<sup>196,197</sup> Long branches in PVC arise from hydrogen abstraction in the CHCl repeat unit within the polymer chain.<sup>198</sup> The polymer transfer constant  $C_P$  is about  $10^{-4}$  or slightly higher for many polymers, such as polystyrene and

<sup>194</sup> Odian, G., *Principles of Polymerization*, 2<sup>nd</sup> ed., Wiley: New York, 1981, 238-242.

<sup>195</sup> Odian, G., *ibid.*, 240.

<sup>196</sup> Odian, G., *ibid.*

<sup>197</sup> Wolf, C.; Burchard, W., *Makromol. Chem.*, 1976, 177, 2519.

<sup>198</sup> Odian, G., *Op. Cit.*, 242.

PMMA.<sup>199,200,201</sup> Assuming a  $C_p$  of  $10^{-4}$ , at 80 % conversion, there should be one branch for every 10,000 monomer units polymerized. At 99 % conversion, one branch would be expected for every 2,000 monomer units polymerized. For many of the polymerizations conducted in this thesis research, chain transfer to polymer may have played a significant role.

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<sup>199</sup> Odian, G., *Principles of Polymerization*, 2<sup>nd</sup> ed., Wiley: New York, 1981, 240.

<sup>200</sup> Brandrup, J.; Immergut, E.H.; Grulke, E.A. Eds., *Polymer Handbook*, 4<sup>th</sup> ed., Wiley: New York, 1999, V, 88.

<sup>201</sup> Corner, T., *Adv. Polm. Sci.*, 1984, 62, 97.